One of the principal difficulties in the silver-dye-bleach process is the selection of suitable dyestuffs for the purpose. Some hundreds of dyestuffs have been suggested, but most of the dyestuffs proposed are unsatisfactory in one or more respects. A principal difficulty is to ensure that the dyestuff employed will not diffuse from the gelatin emulsion layer in which it is incorporated, and various proposals, such as mordanting, have been made to overcome this difficulty. In selecting dyestuffs for use, moreover, it is desirable that they should be bleached rapidly by the bleaching baths employed and also preferable that their inclusion in the emulsion layer should not too seriously reduce the sensitivity of the emulsion. In addition, of course, it is desirable that the dye should approach as closely as possible to the theoretical requirement that, of red, blue and green light it should absorb all of one while fully transmitting or reflecting both of the others.

It is a particular difficulty when using disazo dyes that the bleaching tends to occur by breakdown at one of the azo groups preferentially, resulting in a variation in hue according to the extent of the bleaching. It is important for their use in colour photography that the hue should be unchanged at different levels of bleaching.

The present invention is concerned with the provision of a new class of cyan dyestuffs for use in the silver-dye-bleach process, which approach more closely to the desiderata set forth above.

According to the present invention a process for the production of a cyan dyestuff in a photographic layer comprises including in a light-sensitive gelatin silver halide emulsion layer, or in a plain gelatin layer coated adjacent thereto, a cyan dyestuff of the formula:

\[
A - N = N - \overset{\text{R}}{\text{OH}} \overset{\text{X}}{\text{H}}\]

where A is the residue of an aryl carboxylic alkyl ester of which the alkyl group contains at least 5, and preferably at least 8, carbon atoms, R is a lower alkyl group or a carboxymethyl group, X is a hydroxyl group or an NHR group where R is hydrogen or an R_CO— group (where R is an aryl, alkyl or aryl group or halogen-substituted alkyl or aralkyl or aryl group), and n is 1 or 2, forming a latent silver image in said layer, developing said image, subjecting the developed silver image to treatment which bleaches or removes the silver image and simultaneously bleaches the dyestuff in situ therewith, and removing any residual silver and silver salts from the product.

Methods for the production of the foregoing class of dyestuffs are exemplified later herein. In general terms they are prepared by diazotising a compound of the formula A—NH₂, coupling this with the compound of the formula:

\[
\overset{\text{O}}{\text{R}} \overset{\text{X}}{\text{H}} \overset{\text{N}}{\text{H}}_{2}\]

and diacetylimidazole the product and coupling it with a compound of the formula:

\[
\overset{\text{O}}{\text{H}} \overset{\text{X}}{\text{H}} \overset{\text{SO}_{2}}{\text{H}}_{2}\]
the techniques being those generally used in the production of disazo dyestuffs.

Further according to the invention a process of colour photography comprises a process as just set forth in which the said gelatino-silver-halide layer is sensitive to red light and constitutes one of the layers of a multilayer photographic material which further contains photographic emulsion layers sensitive to blue and green light respectively dyed with yellow and magenta dyestuffs, and the said cyan dyestuff is included in the said red-sensitive layer or in a plain gelatin layer coated adjacent thereto. More particularly the invention provides a process in which the said cyan-dyed layer is layer (b) of an assembly consisting of:

(a) Support layer  
(b) Red-sensitive emulsion layer dyed cyan  
(c) Green-sensitive emulsion layer dyed magenta  
(d) Blue-absorbing filter layer  
(e) Blue-sensitive emulsion layer dyed yellow optionally with plain colloid separating layers between some or all of the adjacent layers recited.

The invention further includes such light-sensitive materials employed in the aforesaid processes, and suitable for variants of those processes, which consist of or include a gelatino silver halide emulsion layer containing a cyan dyestuff as above set forth.

Preferred dyestuffs within the general formula given above are those in which R is a methyl or ethyl group and the sulfonic acid of the middle naphthalene ring is in the 6 or 7 (preferably the 6) position. One of the sulfonic acid groups in the right-hand naphthalene nucleus is preferably in the 4 or 6 position of that nucleus with respect to the 8-hydroxy group and where a second sulfonic acid group is present it is preferably in the 2, 3 or 4 position depending on the position of the first sulfonic acid group. Preferred positions where two sulfonic acid groups are present are the 3:6 and 2:4 positions.

Specific dyestuffs which have been found to be of particular value as set forth in the examples which follow.

The bleaching of the cyan dyestuffs employed in this invention can be affected by any of the types of bleaching bath commonly employed in the silver-dye-bleach process.

The plain use of acid, e.g., hydrobromic or hydrochloric, is effective but is very slow. The inclusion of halide salts has an accelerating effect, but these bleaching baths are still slow. The inclusion of a solvent for silver halide such as thiourea or pyridine has a strongly accelerating effect, and this can be greatly increased by the inclusion of an accelerating substance or catalyst. In these connections reference may be made to British patent specifications Nos. 397,159 and 490,451 for suitable bleaching baths.

The following example, which for simplicity is concerned only with the treatment of a single layer containing the cyan dyestuff, will serve to illustrate the invention.

**EXAMPLE**  
Preparation of the Dyestuffs

**DYESTUFF NO. 1**

36.9 parts of 3-amino-4-phenoxynbenzene-1-carboxylic acid n-decyl ester are dissolved at room temperature in 300 parts of alcohol. 40 parts of concentrated hydrochloric acid are added to the mixture and it is then cooled, whereupon the chlorohydrate precipitates. 40 parts of ice are added and it is diazotised at 0–5° with a concentrated aqueous solution of 6.9 parts of sodium nitrite. After stirring for 2 hours at 0–5° and decomposing the excess nitrous acid, the pale yellowish coloured, clear diazo solution is poured within 2 hours into a suspension of 25.3 parts of 1-amino-2-methoxynaphthalene-6-sulphonic acid and 60 parts of sodium acetate in 500 parts of water and 300 parts of ice. This is performed at 0–5°. The coupling occurs immediately and the colour changes to red. The whole is stirred for 6 hours at this temperature, the acid is then neutralised by the gradual addition of 32 parts of sodium carbonate and the precipitated dyestuff is filtered off under suction. It is washed in the suction filter with a 5% sodium chloride solution.

The brownish-red mattezo dyestuff is dissolved at the boil in 4000 parts of hot water in the presence of 2 g. per litre of the condensation product of dodecyl alcohol and 20 mol of ethylene oxide as dispersing agent, 6.9 parts of sodium nitrite are added, the reaction mixture is cooled to 25° and 40 parts of concentrated hydrochloric acid are added. After stirring for 15 hours at 25–30° a little excess nitrous acid is decomposed with sulphamic acid. The brown-yellowish gelatinous diazo emulsion is then poured at 15–20° into a solution of 36.1 parts of 1-acetylaminod-6-hydroxynaphthalene-3,6-disulphonic acid and 19.3% of sodium nitrite in 100 parts of water and 250 parts of pyridine. The coupling takes place immediately and the colour changes to cyan. Stirring is continued for 4 hours at the same temperature, 600 parts of potassium chloride are added and the dyestuff which precipitates is filtered off under suction. It is washed first with 500 parts of a solution consisting of 50 parts of pyridine, 25 parts of potassium chloride and 350 parts of water, then with 500 parts of pyridine and finally, with 200 parts of acetone, after which it is dried at 80°.

The dyestuff is a blue powder which dissolves in water with a cyan colouration and in concentrated sulphuric acid with a blue colouration.

The 3-amino-4-phenoxynbenzene-1-carboxylic acid decyl ester used as starting component is obtained by condensing 4-chloro-3-nitrobenzene-1-carboxylic acid with excess phenol in the presence of 2.2 mols of potassium hydroxide at temperatures of over 100° C., isolating the free 4-phenoxyn-3-nitrobenzene-1-carboxylic acid, converting this with thionyl chloride into carboxylic acid chloride, reacting the chloride with n-decyl alcohol to form the decyl ester and finally reducing the nitro group to the amino group in aqueous ethyl alcohol.

The following table contains some further disazo dyestuffs which can be used and which can be produced by the method described above. If the starting components are homologous and isomeric or analogous compounds, they are also obtained by the method described above.

**DYESTUFF NO. 2**

36.9 parts of 3-amino-4-phenoxyn-1-carboxylic acid n-decyl ester are diazotised as described in the example of Dyestuff No. 1 and coupled with 25.3 parts of 1-amino-2-
methoxynaphthalene-6-sulphonic acid. This brown-red monoazo dyestuff is dissolved in 4000 parts of boiling water in the presence of 2 g. per litre of the condensation product from 1 mol of dodecyl alcohol and 20 mols of ethylene oxide as dispersing agent, 6.9 parts of sodium nitrite are added, the temperature is reduced to 25° C. and 40 parts of concentrated hydrochloric acid are added. After stirring for 15 hours at 20-25° C. and decomposition of a little excess nitrous acid, the brown-yellow diazo suspension is poured at 20-25° into a solution of 31.9 parts of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid and 80 parts of sodium acetate in 1000 parts of water and 250 parts of pyridine. Coupling occurs immediately and the colour changes to cyan. After stirring for 4 hours at 15-20° C. 400 parts of potassium chloride are added to the dyestuff solution, it is heated to 40° C., the precipitated blue dyestuff is filtered off under suction and washed first with 300 parts of a 20% sodium chloride solution, then with 300 parts of pyridine and finally with 200 parts of acetone. It is then dried in the vacuum at 80° C.

The dyestuff is a blue powder which dissolves in water with a cyan colouration and in concentrated sulphuric acid with a blue colouration.

**DYESTUFF NO. 4**

![DIagram of DYESTUFF NO. 4](image)

341 parts of 3-amino-6-phenoxyn-benzene-1-carboxylic acid-n-octyl ester are diazotised as described in the example of Dyestuff No. 1 and coupled with 1-amino-2-methoxynaphthalene-6-sulphonic acid. The brown-red monoazo dyestuff is dissolved in 4000 parts of boiling water, 6.9 parts of sodium nitrite are added, the temperature is reduced to 25° C. and 40 parts of concentrated hydrochloric acid are added. After stirring for 20 hours and decomposing some excess nitrous acid, the precipitated diazo compound is filtered off under suction and washed with a 20% sodium chloride solution. The diazo compound is pasted in 1000 parts of ice water and the suspension is added in portions at 15-20° C. to a solution of 31.9 parts of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid and 40 parts of sodium acetate in 1000 parts of water and 250 parts of pyridine. Coupling occurs immediately and the colour changes to cyan. After stirring for 4 hours at 15-20° C. 400 parts of potassium chloride are added to the dyestuff solution, it is heated to 40° C., the precipitated blue dyestuff is filtered off under suction and washed first with 300 parts of a 20% sodium chloride solution, then with 300 parts of pyridine and finally with 200 parts of acetone. It is then dried in the vacuum at 80° C.

The dyestuff is a blue powder which dissolves in water with a cyan colouration and in concentrated sulphuric acid with a blue colouration.

**DYESTUFF NO. 3**

![DIagram of DYESTUFF NO. 3](image)

27.7 parts of 4-amino-benzene-1-carboxylic acid-n-decyl ester are suspended in 200 parts of water and 30 parts of hydrochloric acid and diazotised at 0-2° C. with 6.9 parts of sodium nitrite. The clear solution of the diazo compound is then poured at 0-5° C. gradually into a suspension of 25.3 parts of 1-amino-2-methoxynaphthalene-6-sulphonic acid and 60 parts of sodium acetate in 500 parts of water and 500 parts of ice. The coupling occurs immediately and the colour changes to red. The whole is stirred for 6 hours at 0-5° C., the acid is neutralised by the addition of 52 parts of sodium carbonate, the red dyestuff which precipitates is filtered off under suction and washed in the suction filter with a 5% sodium chloride solution.

The brown-red monoazo dyestuff is dissolved in 3000 parts of boiling water, 6.9 parts of sodium nitrite are added, the solution is cooled to 25° C. and 40 parts of concentrated hydrochloric acid are added. After stirring for 20 hours at 20-25° C., a little excess nitrous acid is decomposed with sulphamic acid, the diazo compound is precipitated by the addition of 750 parts of sodium chlor-
<table>
<thead>
<tr>
<th>Dye No.</th>
<th>A</th>
<th>R</th>
<th>X</th>
<th>Position of SO₃H group(s) in end component</th>
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<tbody>
<tr>
<td>5</td>
<td></td>
<td>CH₃</td>
<td>OH</td>
<td>3:6</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>CH₃</td>
<td>NH₃</td>
<td>2:4</td>
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<td>NH₃</td>
<td>4</td>
</tr>
<tr>
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<td>NH₃COCH₃</td>
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<td>4:6</td>
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<td>NH₃</td>
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<td>16</td>
<td>C₆H₅ (tert.)</td>
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<td>NH₃</td>
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<td>NH₃</td>
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<td>NH₃</td>
<td>3:6</td>
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<tr>
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<td>3:6</td>
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Table—Continued

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>A</th>
<th>R</th>
<th>X</th>
<th>Position of SO₂H group(s) in end component</th>
</tr>
</thead>
<tbody>
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<td>22...</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23...</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.33 gms. of dyestuff No. 1 above and 7.4 gms. of dodecyl sodium sulphate are dissolved in 460 ccs. of water. This dye solution is then added to 740 ccs. of a silver chlorobromide emulsion containing 2.6 gms. of silver as silver halide. The mixture is then coated on film base to give a coating weight of 2.7 mgs. of silver per square decimeter.

The dried coating is exposed to light to record an image therein and processed at 68° F. as follows:

1. Develop to a silver image by two minutes' treatment in the following developer:
   - Metal solution
   - Sodium sulphite, cryst
   - Hydroquinone
   - Sodium carbonate, cryst
   - Potassium bromide

   Water to 1 litre.

2. Rinse 30 seconds.
3. Fix in 20% sodium thiosulphate for 3 minutes.
4. Rinse 30 seconds.
5. Harden in 4% formalin.
6. Wash 10 minutes.
7. Dye bleach for 8 minutes in the following bath:
   - Hydrochloric acid (S.G. 1.19) ccs: 100
   - Potassium bromide gms: 12.5
   - Thiourea gms: 10
   - 2:3-dimethyl quinoxaline gms: 0.1

   Water to 1 litre.

8. Wash 5 minutes.
9. Silver bleach for 5 minutes in the following bath:
   - Copper sulphate, cryst
   - Sodium chloride gms: 100
   - Hydrochloric acid, conc. ccs: 50

   Water to 1 litre.

10. Wash 5 minutes.
11. Fix in 20% sodium thiosulphate for 3 minutes.
12. Wash for 10 minutes and dry.

A reverse image in dye is obtained.

Steps 4 and 5 may be omitted if the original emulsion is hardened or provided with a hardened gelatin supercoat.

Similar results are obtained using the other dyestuffs falling within the formula stated, and particularly when using Dyestuffs Nos. 2, 3 and 4 above. When the process is repeated with a similar, but undyed, silver halide emulsion, supercoated on the dyed emulsion, it is found by microscopic examination that substantially none of the dyestuff is removed from the dyed layer and migrates to the undyed layer either on coating the film or on processing.

All of the said dyestuffs are of satisfactory hue, have very good resistance to migration, bleach rapidly and effectively, and are generally of exceptional value in the silver-dye bleach process of colour photography.

This application is divided from application Serial No. 728,065, filed April 14, 1958, now Patent No. 3,002,964. What we claim is:

1. A light-sensitive gelatino silver halide emulsion comprising a cyan dyestuff of the formula:

where A is a radical selected from the class consisting of phenyl- and phenoxyphenyl-carboxylic alkyl esters of which the alkyl group contains at least 5 carbon atoms, R is selected from the class consisting of alkyl groups containing up to 6 carbon atoms and carboxymethyl groups, X is selected from the class consisting of hydroxy, amino, alky carbamylamino, phenylacyl carbamylamido, phenyl carbamylamido, haloalkyl carbamylamido, halo-phenyl-alkyl carbamylamido, halophenyl carbamylamido and halophenoxy-alkyl carbamylamido groups, and n is an integer at least 1 and not more than 2.
where A is a radical selected from the class consisting of phenyl- and phenoxyphenyl-carboxylic alkyl esters of which the alkyl group contains at least 5 carbon atoms, R is selected from the class consisting of alkyl groups containing up to 6 carbon atoms and carboxymethyl groups, X is selected from the class consisting of hydroxy, amino, alkyl carbonylamido, phenylalkyl carbonylamido, phenyl carbonylamido, haloalkyl carbonylamido, halophenylalkyl carbonylamido, halophenyalkyl carbonylamido and halophenoxy-alkyl carbonylamido groups, and n is an integer at least 1 and not more than 2.

4. An emulsion according to claim 1 wherein the cyan dyestuff is:

5. An emulsion according to claim 1 wherein the cyan dyestuff is:

6. An emulsion according to claim 1 wherein the cyan dyestuff is:

7. An emulsion according to claim 1 wherein the cyan dyestuff is:

8. An emulsion according to claim 1 wherein the cyan dyestuff is:

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